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The structure and energetics of  $\text{Cr}(\text{CO})_6$  and  
 $\text{Cr}(\text{CO})_5$

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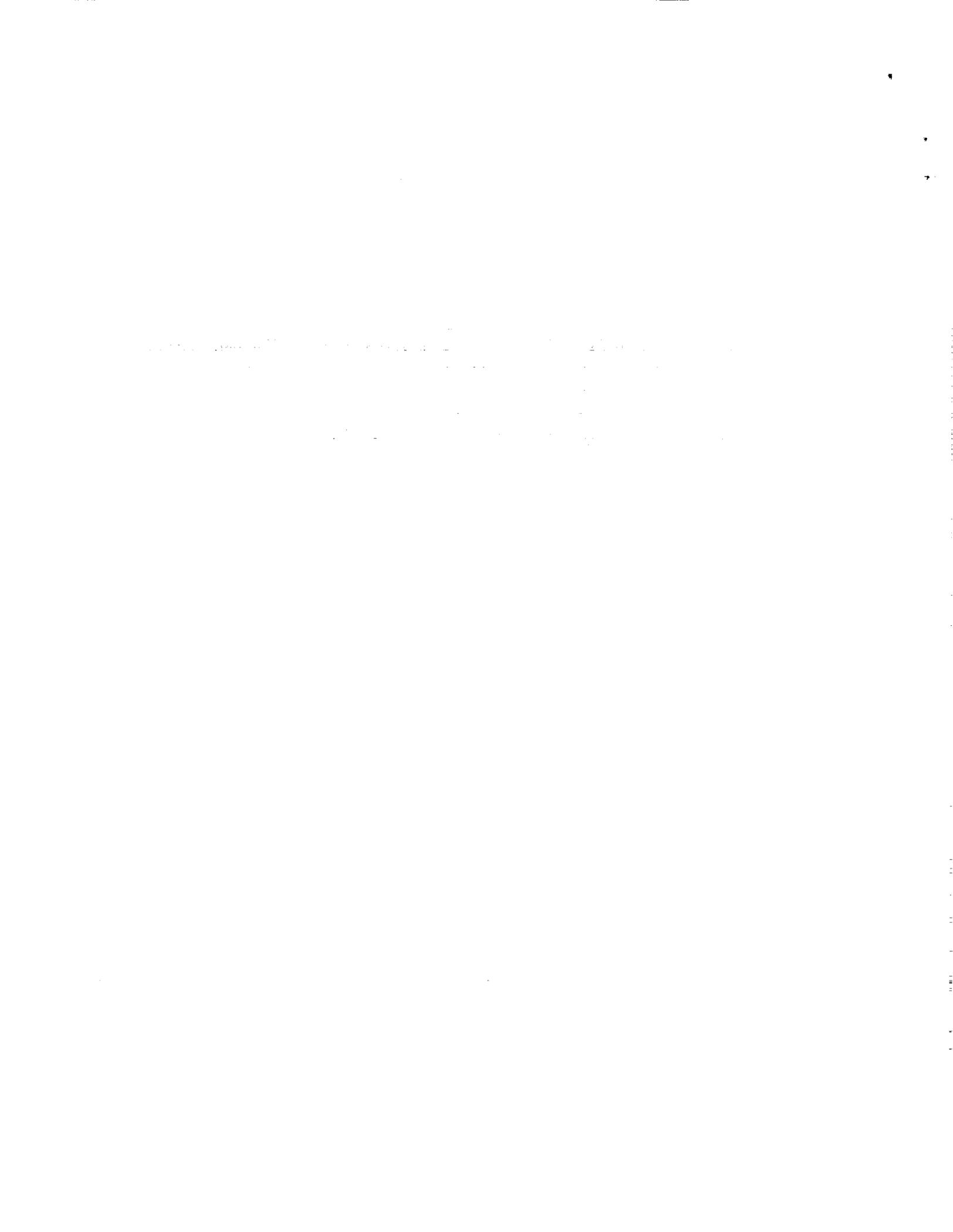
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## Abstract

The geometric structure of  $\text{Cr}(\text{CO})_6$  is optimized at the modified coupled-pair functional (MCPF), single and double excitation coupled-cluster (CCSD) and CCSD(T) levels of theory (including a perturbational estimate for connected triple excitations), and the force constants for the totally symmetric representation are determined. The geometry of  $\text{Cr}(\text{CO})_5$  is partially optimized at the MCPF, CCSD and CCSD(T) levels of theory. Comparison with experimental data shows that the CCSD(T) method gives the best results for the structures and force constants, and that remaining errors are probably due to deficiencies in the one-particle basis sets used for CO. The total binding energies of  $\text{Cr}(\text{CO})_6$  and  $\text{Cr}(\text{CO})_5$  are also determined at the MCPF, CCSD and CCSD(T) levels of theory. The CCSD(T) method gives a much larger total binding energy than either the MCPF or CCSD methods. An analysis of the basis set superposition error (BSSE) at the MCPF level of treatment points out limitations in the one-particle basis used here and in a previous study. Calculations using larger basis sets reduce the BSSE, but the total binding energy of  $\text{Cr}(\text{CO})_6$  is still significantly smaller than the experimental value, although the first CO bond dissociation energy of  $\text{Cr}(\text{CO})_6$  is well described. An investigation of  $3s3p$  correlation reveals only a small effect. In the largest basis set, the total CO binding energy of  $\text{Cr}(\text{CO})_6$  is estimated to be 140 kcal/mol at the CCSD(T) level of theory, or about 86% of the experimental value. The remaining discrepancy between the experimental and theoretical value is probably due to limitations in the one-particle basis, rather than limitations in the correlation treatment. In particular an additional  $d$  function and an  $f$  function on each C and O are needed to obtain quantitative results. This is underscored by the fact that even using a very large primitive set (1042 primitive functions contracted to 300 basis functions), the superposition error for the total binding energy of  $\text{Cr}(\text{CO})_6$  is 22 kcal/mol at the MCPF level of treatment.



# 1 Introduction

The calculation of accurate binding energies for the transition metal carbonyl systems remains a challenging problem for *ab initio* quantum chemistry. These systems are of great interest in many areas of chemistry, ranging from organometallic synthesis to catalysis, surface chemistry, photophysics and thin film deposition of metals (see, for example, references [1, 2, 3] and references therein). The average bond dissociation energy is well known for several saturated transition metal carbonyl systems such as  $\text{Ni}(\text{CO})_4$ ,  $\text{Fe}(\text{CO})_5$ , and  $\text{Cr}(\text{CO})_6$ , but individual carbonyl binding energies are harder to determine experimentally. However, it is the individual bond energies which may be more important in understanding the different processes occurring chemically (see, for example, references [4, 5] and references therein).

From a theoretical viewpoint, the total metal carbonyl binding energy is an important quantity since it provides a good calibration of the theoretical methodology. If this quantity can be computed accurately then individual metal carbonyl binding energies may also be predicted with some confidence. However, if the total binding energy is not well determined, then there may be problems when computing individual binding energies. In addition, the geometrical structure and vibrational frequencies (or force constants) of the saturated carbonyl species are known in several cases, providing another useful calibration of the methods.

Previously, the modified coupled-pair functional (MCPF) method [6] was used to study the systems  $\text{Ni}(\text{CO})_n$ ,  $n = 1, 4$  [7],  $\text{Fe}(\text{CO})_n$ ,  $n = 1, 5$  [4] and  $\text{Cr}(\text{CO})_6$  [4], providing the best *ab initio* binding energies at that time. In general, the total binding energies are too low at this level of treatment — 82% of the experimental value for  $\text{Ni}(\text{CO})_4$  and only 67% and 68% of the experimental value for  $\text{Cr}(\text{CO})_6$  and  $\text{Fe}(\text{CO})_5$ , respectively, without correcting for basis set superposition error (BSSE). For  $\text{Fe}(\text{CO})_5$  the first bond dissociation energy was well determined, whereas subsequent bond dissociation energies were harder to determine, so that only a lower bound of 5 kcal/mol could be given for the last bond dissociation energy. In contrast, the bond distances and force constants were generally in better agreement with the experimental data than would be expected on the basis of the binding energies alone. For the cases of  $\text{Fe}(\text{CO})_5$  and  $\text{Cr}(\text{CO})_6$  the possible sources of error in the binding energies were discussed in terms of the difficulty in accurately describing the change in metal *3d* configuration upon forming the carbonyl complex and the loss of the high-spin coupling exchange energy in the molecule.

Recently, the single and double excitation coupled-cluster (CCSD) method that

includes a perturbational estimate for connected triple excitations (CCSD(T)) [8] has been used to study  $\text{Ni}(\text{CO})_n$ ,  $n = 1, 4$ , and  $\text{Ni}(\text{C}_2\text{H}_4)$  [9]. This CCSD(T) approach yielded good results in all cases, giving an additional 17.5 kcal/mol of binding energy for  $\text{Ni}(\text{CO})_4$  compared with the MCPF result. After correction for BSSE, the total binding energy of  $\text{Ni}(\text{CO})_4$  was 89% of the experimental value. The remaining errors were shown to be largely due to deficiencies in the one-particle basis set, because use of a very large one-particle basis set for NiCO yielded an additional 3.5 kcal/mol in the binding energy. If this correction is applied to  $\text{Ni}(\text{CO})_4$  (for each CO), the experimental result would be reproduced almost exactly.

In the previous work [4], we compared the results of the MCPF calculations to other theoretical work, such as  $X\alpha$  [10], density functional [11] and SDCl calculations [12]. A detailed analysis of the energetics and electronic structure of  $\text{Cr}(\text{CO})_6$  was recently carried out by Kunze and Davidson [13], at the SCF level of theory in a large one-particle basis set. However, even in a large one-particle basis set, at the SCF level of treatment  $\text{Cr}(\text{CO})_6$  is still unbound by 111 kcal/mol [13] relative to the ground state Cr and CO fragments, illustrating the importance of electron correlation for the total binding energy. Regarding  $\text{Cr}(\text{CO})_5$  and the first bond dissociation energy of  $\text{Cr}(\text{CO})_6$ , there is some previous work which has been carried out at a qualitative level in small basis sets. We note in particular the work of Hay [14] on different electronic states of  $\text{Cr}(\text{CO})_5$  and Sherwood and Hall [15] on the dissociation of a single carbonyl from  $\text{Cr}(\text{CO})_6$ . In the former work, SDCl calculations in a small one-particle basis at fixed bond lengths found  $\text{Cr}(\text{CO})_5$  to have a  $^1A_1$  ground state of  $C_{4v}$  symmetry (square pyramid). The  $D_{3h}$  structure (trigonal bipyramid) was about 9 kcal/mol higher in energy. The latter work found the first bond dissociation energy of  $\text{Cr}(\text{CO})_6$  to be 49.8 kcal/mol at the SCF level of theory. In addition, Demuyneck *et al.* [16] have studied the interaction of a rare-gas atom with  $\text{Cr}(\text{CO})_5$ , at the SCF level of theory in small basis sets, using experimental bond distances from  $\text{Cr}(\text{CO})_6$ . They found the ground state of  $\text{Cr}(\text{CO})_5$  to be  $^1A_1$  in  $C_{4v}$  symmetry, with an equatorial to axial CO angle of around  $92^\circ$ . More recently, Pacchioni [17] has carried out some SCF calculations on  $\text{Cr}(\text{CO})_5$  in a study of  $\text{Cr}(\text{CO})_5\text{H}_2$  and  $\text{Cr}(\text{CO})_4(\text{H}_2)_2$ , and Nilson *et al.* [18] have carried out some limited MCSCF calculations in a combined experimental and theoretical study of the photoelectron spectrum of  $\text{Cr}(\text{CO})_6$ . However, these studies did not address the binding energies or geometric structures of  $\text{Cr}(\text{CO})_5$  or  $\text{Cr}(\text{CO})_6$ .

In the current work we have used the MCPF, CCSD and CCSD(T) approaches to study  $\text{Cr}(\text{CO})_6$  and  $\text{Cr}(\text{CO})_5$  in the same basis as used previously [4] and in sig-

nificantly larger basis sets. The geometric structure of  $\text{Cr}(\text{CO})_6$  is optimized at the CCSD and CCSD(T) levels of theory and the force constants for the totally symmetric representation are determined. The previously published work which gave the structure and Cr-C totally symmetric force constant of  $\text{Cr}(\text{CO})_6$  using the MCPF approach is extended to include the C-O totally symmetric force constant and the coupling term. The geometry of  $\text{Cr}(\text{CO})_5$  is partially optimized at the MCPF, CCSD and CCSD(T) levels of theory.

The first bond dissociation energy, that is the energy required for the process



is known experimentally, as well as the total binding energy of  $\text{Cr}(\text{CO})_6$ , the energy required for the process



We have looked at both these processes in the current work, including a correction for BSSE and the effect of semi-core  $3s3p$  correlation.

In § 2 we discuss the methods used, including the one-particle and  $n$ -particle treatments. In § 3 we present the results and discussion, first giving the geometrical structure and force constants for  $\text{Cr}(\text{CO})_6$  (§ 3.1), then the geometrical structure for  $\text{Cr}(\text{CO})_5$  (§ 3.2), and finally the results for the bond dissociation energies (§ 3.3).

## 2 Methods

The standard Cr basis is the  $(14s\ 9p\ 5d)$  primitive Gaussian basis set of Wachters [19], contracted to  $[8s\ 4p\ 3d]$  using his contraction scheme 2. Two diffuse  $p$  functions, as recommended by Wachters, and the diffuse  $d$  function of Hay [20] are added, yielding a final basis set of the form  $(14s\ 11p\ 6d)/[8s\ 6p\ 4d]$ . The standard C and O basis sets are  $[4s\ 3p]$  contractions of the  $(9s\ 5p)$  primitive Gaussian set of van Duijneveldt [21], with the  $s$  and  $p$  spaces contracted (5211) and (311) respectively. In all calculations, except those done using CADPAC (see below), only the pure spherical harmonics are used.

For the larger basis set calculations on  $\text{Cr}(\text{CO})_6$  and  $\text{Cr}(\text{CO})_5$ , we use a  $(13s\ 8p\ 6d)$  primitive basis set for C and O, contracted using the Atomic Natural Orbital (ANO) procedure [22]. This basis set is derived from the  $(13s\ 8p)$  set of

van Duijneveldt [21] supplemented with polarization functions as prescribed in reference [22] and contracted to  $[4s\ 3p\ 1d]$  for use in  $\text{Cr}(\text{CO})_6$  and  $\text{Cr}(\text{CO})_5$ .

For the valence correlation calculations on  $\text{Cr}(\text{CO})_6$  and  $\text{Cr}(\text{CO})_5$  we have used two molecular basis sets which we term "small" and "large". The "small" basis set consists of the standard Wachters and van Duijneveldt sets described above and is the same basis used previously [4], containing 202 contracted functions for  $\text{Cr}(\text{CO})_6$ . We use this basis set to compare results at the MCPF, CCSD and CCSD(T) levels of treatment. The "large" basis set is the Wachters metal set supplemented with a  $(3f)/[1f]$  contracted function (see reference [23]), and the  $[4s\ 3p\ 1d]$  ANO set on C and O, giving 269 contracted basis functions for  $\text{Cr}(\text{CO})_6$ . With this basis set we use only the MCPF method for the geometry optimization of  $\text{Cr}(\text{CO})_6$ . For the CCSD(T) method, the calculation was carried out at a single point derived from a combination of the small basis MCPF and CCSD(T) results, and the large basis MCPF results.

It is well known that all the valence electrons must be correlated in metal-carbonyl complexes in order to compute accurate binding energies [7, 24]. However, as discussed by Kunze and Davidson [13], in  $\text{Cr}(\text{CO})_6$  there is a significant overlap between the CO  $5\sigma$  electrons and the  $3p$  electrons of Cr. Therefore, we have also investigated the effect of correlating the chromium semi-core  $3s3p$  electrons *and* all the valence electrons in  $\text{Cr}(\text{CO})_6$ . We denote the calculations as "valence only" if only the valence electrons were correlated, or " $3s3p + \text{valence}$ " if both the  $3s3p$  and valence electrons are correlated.

For the  $3s3p + \text{valence}$  calculations we initially used a basis set derived from the "small" set discussed above, with the inner  $3p$  functions on Cr more flexibly contracted and the addition of two contracted  $f$  functions to Cr, but retaining the  $[4s\ 3p]$  segmented basis set on CO. However, due to the unbalanced nature of this basis, the superposition error was increased considerably and the binding energies were anomalous. Therefore, we instead used the  $(20s\ 12p\ 9d)$  primitive set of Partridge [25], optimized for the  $^5D$  state of Cr. This was contracted in a flexible way to  $[(3 + 6)s\ (2 + 4)p\ (1 + 4)d]$ , with the outermost six  $s$ , four  $p$  and four  $d$  functions uncontracted. The inner three  $s$ , two  $p$  and one  $d$  functions are generally contracted based on the  $1s, 2s, 3s, 2p, 3p$  and  $3d$  SCF atomic orbitals, respectively [25]. This basis is supplemented with two even-tempered diffuse  $p$  functions to describe the  $4p$  orbital, with exponents of 0.127803 and 0.051121, and a diffuse  $d$  function with exponent 0.045794 [25]. In addition, we use a  $(4f)/[3f]$  set of functions, based on the  $(3f)$  primitive set of the "large" basis referenced above and a  $(1f)$  primitive function optimized for  $3p$  correlation in the Cr atom [26]. The contraction coefficients

are taken from the natural orbitals of an MCPF calculation on the  ${}^7S$  state of the Cr atom which correlates the  $3s$ ,  $3p$ ,  $3d$  and  $4s$  electrons. The final Cr basis is of the form  $(20s\ 14p\ 10d\ 4f)/[(3+6)s\ (2+6)p\ (1+5)d\ 3f]$  and is combined with the  $[4s\ 3p\ 1d]$  ANO basis set for CO to give the "large  $3s3p$ " basis set for  $\text{Cr}(\text{CO})_6$ . This basis consists of 1042 primitive Gaussian functions and 300 contracted functions. The exponents and contraction coefficients for the large  $3s3p$  Cr basis are given in the Appendix.

As discussed above, the MCPF, CCSD and CCSD(T) methods are used, correlating 56 electrons in  $\text{Cr}(\text{CO})_5$  and 66 electrons for the valence correlation treatment of  $\text{Cr}(\text{CO})_6$ , or 74 electrons when  $3s3p$  correlation is included. As noted in previous work, the use of a size-extensive method is essential when treating this many electrons in the correlation procedure. The reference function is an SCF single configuration computed with full symmetry and equivalence restrictions. For the CCSD/CCSD(T) calculations on the  ${}^7S$  state of the Cr atom we use the open-shell coupled-cluster method [27] to compute the atomic energy used in the binding energy calculation for the (closed shell) molecular species.

For  $\text{Cr}(\text{CO})_6$  we consider only the  ${}^1A_{1g}$  state with  $3d$  occupation  $t_{2g}^6$  in  $O_h$  symmetry. At the SCF level of theory the geometry was optimized using analytic gradient techniques (using the small basis), under the constraint of  $O_h$  symmetry, and harmonic frequencies were computed. At the correlated level the geometry was optimized by fitting energy points with displacements of  $0.025\ a_0$  in the Cr-C bond and  $0.010\ a_0$  in C-O, first performing independent Cr-C and C-O displacements, and then combined displacements to determine coupling effects. In general, about 14 points were used to determine the two bond lengths and three force constants for the totally symmetric representation (see reference [28], Table IX, for a definition of the symmetry internal coordinates and force constants).

Experimentally, matrix-isolated  $\text{Cr}(\text{CO})_5$  has been shown to be of  $C_{4v}$  symmetry, obtained from  $\text{Cr}(\text{CO})_6$  by the removal of a single CO moiety without further geometrical rearrangement (see references [29]–[33]). This gives a  ${}^1A_1$  state with occupation  $e^4b_2^2$ . There is also a  $D_{3h}$  structure (analogous to  $\text{Fe}(\text{CO})_5$ ) which has a  ${}^3A'_2$  ground state with  $e''^4e'^2$  occupation (see the work of Hay [14] for a general discussion of the electronic structure of  $\text{Cr}(\text{CO})_5$ ). Both structures were fully optimized at the SCF level of theory in the small basis, and were found to be almost degenerate, with the  $C_{4v}$  structure lower by only 0.8 kcal/mol. Previously, Hay [14] found the  $D_{3h}$  structure to be lower by 2.8 kcal/mol, at the SCF level of theory, with a minimal basis on CO (and without geometry optimization). Using a larger  $[3s\ 2p]$

CO basis (also without full geometry optimization) Demuynck *et al.* [16] found the  $C_{4v}$  structure to be lower by around 10 kcal/mol at the SCF level of theory. In addition, at the SDCI level the  $C_{4v}$  structure was lowered by around 12 kcal/mol [14] compared to the  $D_{3h}$  structure. Therefore, in the current work only the  $C_{4v}$  structure was further (partially) optimized including electron correlation at the MCPF, CCSD and CCSD(T) levels of theory. The bond angles were fixed at the SCF values and the C-O distances were fixed at a value deduced from a combination of the SCF optimized values and the correlated results for  $\text{Cr}(\text{CO})_6$  (see § 3.1 and § 3.2 later). The Cr-C bonds may be separated into “axial” and “equatorial”, with the axial bond along the  $C_4$  axis. For the CCSD and CCSD(T) methods only the equatorial bond distance was optimized, the axial distance again being fixed at a value derived from the SCF results for  $\text{Cr}(\text{CO})_5$  and  $\text{Cr}(\text{CO})_6$  and the correlated results for  $\text{Cr}(\text{CO})_6$ . We note that the binding energy is relatively insensitive to the Cr-C bond distance and the bond angles.

The calculations were performed on an IBM3090/300J and IBM RISC SYSTEM/6000 computers at the IBM Almaden Research Center, and on the the NASA Ames Central Computer Facility and NAS facility CRAY Y-MP computers. The SCF geometry optimizations and harmonic frequency calculations on  $\text{Cr}(\text{CO})_5$  and  $\text{Cr}(\text{CO})_6$  were performed using the CADPAC [34] program system. The integrals for the correlated calculations were evaluated with the MOLECULE [35] and SEWARD [36] programs. The SCF/MCPF calculations were performed using the SWEDEN [37] program system, and the closed shell CCSD/CCSD(T) calculations were performed using the TITAN [38] program system. The open-shell CCSD/CCSD(T) calculations were performed using the code of Scuseria [27].

## 3 Results and Discussion

### 3.1 The geometric structure and force constants of $\text{Cr}(\text{CO})_6$

The bond lengths for  $\text{Cr}(\text{CO})_6$  are given in Table 1. The small basis results using the MCPF method are slightly different to those published previously [4], due to the use of a finer grid for the fitting in the current work. The Cr-C distance at the SCF level is much too long, as expected, and electron correlation reduces this distance significantly. Interestingly, the CCSD approach yields a shorter bond distance than MCPF (for isolated CO, the MCPF approach is *between* CCSD and CCSD(T) [39]), and adding the triples correction has a significant effect, so that the CCSD(T) method

yields a Cr–C bond distance which is only about  $0.05 a_0$  longer than experiment [40, 41]. As found using the MCPF approach in the previous work, the C–O distance is significantly too long at the correlated level when compared to the experimental data. However, this is largely a basis set effect. Using the isolated C–O bond distances from reference [39] in the  $[4s\ 3p]$  segmented basis, we find that the error is less than  $0.01 a_0$  for all three methods after correcting for basis set effects.

Using the large basis set at the MCPF level gives significantly improved results. The Cr–C distance is about  $0.03 a_0$  shorter and the C–O distance is  $0.05 a_0$  shorter, which again is mainly a basis set effect found in isolated CO [39]. Applying these changes to the CCSD(T) distances in the small basis, we estimate a value for  $r(\text{Cr–C})$  of about  $3.64 a_0$  and  $r(\text{C–O})$  of about  $2.18 a_0$  at the CCSD(T) level, in reasonable agreement with the experimental data. In isolated CO, the bond distance decreases by  $0.02 a_0$  on going from the  $[4s\ 3p\ 1d]$  basis to a very large basis set [39], which accounts almost entirely for the remaining discrepancy with experiment for  $\text{Cr}(\text{CO})_6$ . Thus it seems that improvements in the one-particle basis set for  $\text{Cr}(\text{CO})_6$  would yield very good agreement with experiment at the CCSD(T) level of treatment, but that even with the  $[4s\ 3p]$  basis the *change* in the C–O bond length on going from isolated CO to  $\text{Cr}(\text{CO})_6$  is well described.

The force constants for  $\text{Cr}(\text{CO})_6$  are given in Table 2, and are consistent with the bond length results discussed above. The Cr–C force constant,  $F_{22}$ , is improved on going from the MCPF level to CCSD and CCSD(T) levels of treatment, as found for  $r(\text{Cr–C})$ . In the large basis, the MCPF value for  $F_{22}$  is increased significantly so that we may estimate a value of around  $2.5 \text{ aJ}/\text{\AA}^2$  at the CCSD(T) level in the large basis, which is to be compared with the experimental value of  $2.44 \text{ aJ}/\text{\AA}^2$  [28].

The C–O force constant,  $F_{11}$ , is too small in the small basis for all three methods, consistent with the isolated CO results of reference [39] in the  $[4s\ 3p]$  basis. The force constant is smaller than in isolated CO, consistent with the longer bond C–O distance in  $\text{Cr}(\text{CO})_6$ . In the large basis  $F_{11}$  is markedly better, mainly due to improvement in the treatment of the isolated CO (as noted for  $r(\text{C–O})$ ), although the MCPF value is larger than experiment in the large basis. However, the CCSD(T) method yields an  $F_{11}$  value which is significantly smaller than the MCPF value in the small basis, and we may estimate a value of  $18.0 \text{ aJ}/\text{\AA}^2$  for the CCSD(T) method in the large basis, which compares well with the experimental value of  $18.11 \text{ aJ}/\text{\AA}^2$  [28].

The coupling term  $F_{12}$  is too small at all levels of theory, and interestingly is smaller in the large basis, and smaller at the CCSD(T) level than MCPF. It is difficult to predict how this term will change with higher levels of theory — however,

given the relatively large error bar on the experimental value and the fact that the experimental value may be significantly affected by anharmonic effects, the results are reasonable.

Overall, the theoretical results for geometry and force constants are in good agreement with experiment within the limitations of the one-particle basis set, and the CCSD(T) method yields consistently better results than MCPDF.

### 3.2 The geometric structure of $\text{Cr}(\text{CO})_5$

The results for the structure of  $\text{Cr}(\text{CO})_5$  are given in Table 3, in the small basis set. As noted above, matrix-isolated  $\text{Cr}(\text{CO})_5$  is known to have  $C_{4v}$  symmetry, with an angle  $\angle C_{ax}CrC_{eq}$  of about  $93^\circ$  [33], although the  $D_{3h}$  structure has also been proposed under certain conditions [42] (see also reference [33]). No gas-phase structural information is known.

We first look briefly at the  $D_{3h}$  structure in Table 3. This is the same structure as found for  $\text{Fe}(\text{CO})_5$  — a pentagonal bipyramid. However, the *equatorial* Cr–C bond distance is very long at the SCF level of treatment compared with the axial distance, whereas in  $\text{Fe}(\text{CO})_5$  the *axial* Fe–C distance is much longer than the equatorial distance (Luthi *et al.* [43]). This may be understood from the *d*-orbital occupations of the two species. In  $\text{Cr}(\text{CO})_5$ , the occupation of the  $^3A'_2$  state is predominantly  $d_{xz}^2 d_{yz}^2 d_{x^2-y^2}^1 d_{xy}^1$ , (see Hay [14], for example), giving the axial CO group (along *z*) a greater bonding interaction than the equatorial groups. In  $\text{Fe}(\text{CO})_5$ , the configuration is  $d_{xz}^2 d_{yz}^2 d_{x^2-y^2}^2 d_{xy}^2$ , with only an empty  $d_{z^2}$  orbital, and in this case the equatorial groups are favoured over the axial groups. However, when extensive electron correlation is included, we expect the equatorial Cr–C distance would be significantly shortened, as found for the axial Fe–C distance in  $\text{Fe}(\text{CO})_5$ . The C–O bond distances reflect the different Cr–C distances also — at the SCF level of theory the axial CO has a much stronger interaction with the Cr atom and so has a longer C–O bond distance. The equatorial CO has a weaker interaction and so a shorter C–O bond distance.

We now consider the  $C_{4v}$  structure, from the results in Table 3. At the SCF level of theory, the equatorial Cr–C distance is very similar to that in  $\text{Cr}(\text{CO})_6$ , whereas the axial distance is slightly shorter, as may be expected with the removal of the opposing “axial” CO in  $\text{Cr}(\text{CO})_6$ . The angle  $\angle C_{ax}CrC_{eq}$  is in good agreement with the experimental estimate of  $93^\circ$ , and the  $92^\circ$  value of Demuynck *et al.* [16]. There are also semi-empirical estimates of  $93^\circ$  [44] and  $93.5^\circ$  [45] for this angle. The angle

$\angle \text{CrC}_{eq}\text{O}_{eq}$  is very close to  $180^\circ$ , as may be expected, and the C–O bond distances are both close to the C–O distance in  $\text{Cr}(\text{CO})_6$ . Thus at the SCF level of theory,  $\text{Cr}(\text{CO})_5$  is only slightly perturbed from the  $\text{Cr}(\text{CO})_6$  structure. Given this fact, at the correlated level of theory we fix the C–O distances based on the  $\text{Cr}(\text{CO})_6$  correlated results. For the CCSD/CCSD(T) calculations we use a compromise distance which should be suitable for both methods. As noted previously, the angles are fixed at the SCF values.

At the MCPF level of theory, both Cr–C bond distances are fully optimized. In this case the axial bond distance contracts more than found in  $\text{Cr}(\text{CO})_6$  (see Table 1) and the equatorial distance a little less than in  $\text{Cr}(\text{CO})_6$ . At the CCSD and CCSD(T) levels of theory, the axial bond contracts even further, which may be expected based on the  $\text{Cr}(\text{CO})_6$  results of Table 1. (In this case we did not optimize the equatorial bond distance, fixing it at about the  $\text{Cr}(\text{CO})_6$  value). The additional contraction of the axial bond distance at the correlated level of theory is a consequence of configurational mixing of a low-lying  $3d4p$  hybrid orbital in  $\text{Cr}(\text{CO})_5$ , which is much higher lying in  $\text{Cr}(\text{CO})_6$ , so that  $\text{Cr}(\text{CO})_5$  is more poorly described at the SCF level than  $\text{Cr}(\text{CO})_6$ . This may be seen in the  $\mathcal{T}_1$  diagnostic [46] from the coupled-cluster calculations, for example, which is around 0.032 in  $\text{Cr}(\text{CO})_6$  and around 0.038 in  $\text{Cr}(\text{CO})_5$ .

A full optimization of both the Cr–C and C–O distances of  $\text{Cr}(\text{CO})_5$  at the CCSD(T) level in a larger basis is probably desirable — however, given the paucity of experimental data on the structure of  $\text{Cr}(\text{CO})_5$ , this is postponed to a later date. An estimate of the optimal geometry was made by combining the  $\text{Cr}(\text{CO})_6$  and  $\text{Cr}(\text{CO})_5$  results presented here, and is given in the footnotes to Table 7.

### 3.3 Energetics

#### 3.3.1 Basis set superposition error

In the previous work, we did not compute the BSSE associated with the total binding energy of  $\text{Cr}(\text{CO})_6$ , although in earlier work on  $\text{NiCO}$  [47],  $\text{Ni}(\text{CO})_2$  [7] and  $\text{TiCO}$  [24], it was found that the BSSE and basis set expansion effects tended to cancel to a large extent. However, the recent work of Blomberg *et al.* [9] on  $\text{Ni}(\text{CO})_4$  indicated a large superposition error in a basis set larger than the small basis used here. Therefore we have considered the BSSE question in some detail. Blomberg *et al.* found that the CCSD/CCSD(T) and MCPF methods gave similar results for the BSSE correction in  $\text{Ni}(\text{CO})_4$  (around 8% larger for the CCSD(T) method compared to MCPF), so

that in the current work we use only the MCPF approach for the computation of the BSSE, using the full counterpoise method [48]. The results are given in Tables 4 and 5, where we break down the various contributions for the different systems and basis sets. Total energies for various BSSE calculations are given in the Appendix.

For the total binding energy of  $\text{Cr}(\text{CO})_6$  there is a large superposition error in the small basis, as shown in entry (1) of Table 4. At the correlated level of theory, the superposition error is around three times the SCF result (this seems to roughly hold for all the results presented in Table 4). The dominant contribution is from CO, with about 4 kcal/mol/CO, with a comparatively small contribution from the Cr atom. The overall BSSE correction of 28 kcal/mol is a very large correction to a total computed binding energy of about 110 kcal/mol. Thus larger basis sets are essential in order to compute reliable energetic quantities for  $\text{Cr}(\text{CO})_6$ .

In the large basis for  $\text{Cr}(\text{CO})_6$  (entry (2)) the superposition error is about half that of the small basis, at both the SCF and MCPF levels of theory. The SCF result is very good, slightly lower than the recent value of 7 kcal/mol given by Kunze and Davidson [13], even though the total energy of  $\text{Cr}(\text{CO})_6$  is about 0.01 a.u. higher than their value. At the MCPF level of theory, the CO contribution to the superposition error is reduced to about 2 kcal/mol/CO, and the Cr contribution is reduced from the small basis result. Thus the correction is quite reasonable when viewed on a per CO basis. However, the overall correction for six CO ligands, although much improved from the small basis, is still large.

For a given one particle basis the computed BSSE will be an upper bound to the true correction. Naively, one might then expect that calculations in a larger basis will reduce the BSSE. However, this is not usually true. If the ghost basis contains no functions which account for the deficiencies in the fragment basis, then the computed superposition error will be zero, but this does not mean that there are no deficiencies in the fragment basis. Thus increasing the size of the ghost basis will increase the superposition error for a given fragment. In the current work using the large  $3s3p$  basis (entries (3) and (4)), this is the case. There is an overall *increase* in superposition error at both the SCF and MCPF levels of theory, when compared with entry (2), which has the same basis on CO but a smaller basis on Cr. The Cr portion of the superposition error is reduced to almost nothing at the SCF level, and is significantly reduced at the correlated level. However, a side effect of using a large, flexibly contracted basis set on Cr is to increase the superposition error for the  $(\text{CO})_6$  fragment significantly — the SCF superposition error has increased by nearly 3 kcal/mol and the MCPF superposition error has increased by around 8 kcal/mol,

when compared with the results in entry (2). Thus our superposition error at the SCF level is slightly larger than the 7 kcal/mol given by Kunze and Davidson [13], even though our total energy is now almost 0.05 a.u. lower than their value. These results indicate that even at the SCF level we need a larger basis — probably an additional contracted  $d$  function on each C and O. At the correlated level, the superposition error is again increased by almost three times the increase at the SCF level of theory. Thus, to reduce the superposition error significantly at the correlated level, the  $[4s\ 3p\ 2d\ 1f]$  ANO basis should be used on CO and would probably give very good results when combined with a larger Cr basis. However, as noted previously, this leads about 440 basis functions which is too large at the current time.

For the first bond dissociation energy of  $\text{Cr}(\text{CO})_6$  (equation (1)), the superposition error may be computed in two ways — indirectly as the difference between the superposition errors for the total binding energy of  $\text{Cr}(\text{CO})_6$  and the total binding energy of  $\text{Cr}(\text{CO})_5$ , or directly using the appropriate fragments for equation (1).

From entry (1) in Table 5, we see that the BSSE for the total CO bond dissociation energy of  $\text{Cr}(\text{CO})_5$  is qualitatively similar to that for  $\text{Cr}(\text{CO})_6$  (entry (1) of Table 4), being roughly proportional to the number of CO ligands. For the first bond dissociation energy, we subtract the  $\text{Cr}(\text{CO})_6$  and  $\text{Cr}(\text{CO})_5$  numbers (entry (1) in Tables 4 and 5, respectively) giving a superposition error of 1.7 kcal/mol at the SCF level and 5.6 kcal/mol at the MCPF level. Alternatively, entry (2) of Table 5 gives the superposition error computed directly from fragments derived from equation (1). The correction is much larger in this case, at both the SCF and MCPF levels of theory. The difference between the two corrections serves to illustrate the uncertainty in the estimation of BSSE via the counterpoise method.

In the large basis, we have only computed the BSSE via the indirect method. Entry (3) in Table 5 gives the results for the total binding energy of  $\text{Cr}(\text{CO})_5$ . When compared with entry (1), the reduction in BSSE is similar to  $\text{Cr}(\text{CO})_6$  (entries (1) and (2) of Table 4). From these results, the BSSE for the first bond dissociation energy in the large basis is 0.7 kcal/mol at the SCF level and 2.3 kcal/mol at the MCPF level of treatment.

These results emphasize several points. The computed superposition correction must be treated with caution, and may not be a true indication of deficiencies in the fragment basis. Also, a lower total energy does not necessarily imply a lower superposition error. Finally, different methods of computing the superposition error may give quite different corrections. Nevertheless, within a particular one particle basis, the counterpoise method should give some idea of possible errors in the com-

puted binding energies. Only a series of calculations using larger and larger basis sets can give a more accurate estimate of basis set limitations, but this is very difficult for  $\text{Cr}(\text{CO})_6$  at the correlated level of treatment.

### 3.3.2 The total CO binding energy of $\text{Cr}(\text{CO})_6$ and $\text{Cr}(\text{CO})_5$

The total binding energies for  $\text{Cr}(\text{CO})_6$  and  $\text{Cr}(\text{CO})_5$  are given in Tables 6 and 7. We give both the total binding energy and the binding energy per CO molecule, with and without the correction for BSSE. For reference purposes, the total energies for several  $\text{Cr}(\text{CO})_6$  calculations are given in the Appendix. In the small basis, the CCSD method yields a binding energy which is slightly smaller than MCPF. The contribution from connected triple excitations (T) is very large, about 36 kcal/mol in  $\text{Cr}(\text{CO})_6$  compared with 30 kcal/mol in  $\text{Ni}(\text{CO})_4$  [9]. Thus the contribution per CO is about 1.5 kcal/mol smaller in  $\text{Cr}(\text{CO})_6$  than in  $\text{Ni}(\text{CO})_4$ . In  $\text{Cr}(\text{CO})_5$  the triples contribution is about 31.5 kcal/mol and so the contribution per CO is slightly larger than in  $\text{Cr}(\text{CO})_6$  but smaller than  $\text{Ni}(\text{CO})_4$ . After correcting for BSSE, the total binding energy is reduced significantly, as expected.

In the large basis at the MCPF level of theory, the total binding energy of  $\text{Cr}(\text{CO})_6$  is *reduced* by almost 10 kcal/mol compared to the small basis, which is undoubtedly due to the large reduction in BSSE. An analogous, though smaller, effect was found for  $\text{NiCO}$  [9] and  $\text{NiN}_2$  [47]. However, after correction for BSSE, the large basis result is about 3 kcal/mol *larger* than the small basis result. Similarly the CCSD and CCSD(T) binding energies are reduced in the large basis set, although the CCSD(T) value is reduced less than MCPF. The triples correction to the CCSD binding energy is now even larger, at 41 kcal/mol, but is still smaller per CO than in  $\text{Ni}(\text{CO})_4$ . After correction for BSSE, it is easily seen that the CCSD(T) method has yielded more binding energy as a function of the increase in the basis set size than has the MCPF method, as found for  $\text{NiCO}$  [9].

In the large  $3s3p$  basis set, we have computed the total binding energy including both  $3s3p$  and valence correlation, and only the valence correlation, using the MCPF method. The effect of using a larger Cr basis is 6.1 kcal/mol at the valence level, whereas the effect of  $3s3p$  correlation is only 3.8 kcal/mol, after correction for BSSE. Thus the total binding energy is increased by around 10 kcal/mol using the large  $3s3p$  basis set and including  $3s3p$  correlation. This effect may increase at the CCSD(T) level, recalling the results given above for the small and large basis sets. Relativistic effects, which were not included here, are expected to contribute around 3–4 kcal/mol to the total binding energy of  $\text{Cr}(\text{CO})_6$  [4, 9].

From the MCPF results in the small, large and large  $3s3p$  basis sets, and the CCSD(T) results in the small and large basis sets, we estimate a CCSD(T) value of about 140 kcal/mol in the large  $3s3p$  basis, including the effect of  $3s3p$  correlation and a small relativistic correction. This is around 86% of the experimental value, similar to the value of 89% found for  $\text{Ni}(\text{CO})_4$  in a basis of similar size to our large basis, at the CCSD(T) level of theory. As discussed in § 1, for  $\text{NiCO}$  the use of a very large basis gave an additional 3.5 kcal/mol of binding energy compared to a smaller basis set, at the CCSD(T) level of theory. Recalling the large BSSE correction to the binding energy in our largest basis set, this indicates that the remaining discrepancy for  $\text{Cr}(\text{CO})_6$  is probably due to one-particle basis set limitations, and the use of a basis such as the  $[4s\ 3p\ 2d\ 1f]$  ANO set for CO with the CCSD(T) method would give very good results.

For the total binding energy of  $\text{Cr}(\text{CO})_5$  (Table 7) we obtain results similar to  $\text{Cr}(\text{CO})_6$  on going from MCPF to CCSD(T), although the total increase in binding energy is lower. The binding energy per CO molecule is seen to be about 3–4 kcal/mol larger for  $\text{Cr}(\text{CO})_6$  than  $\text{Cr}(\text{CO})_5$ . Again in the large basis set the binding energy is reduced significantly compared to the small basis set result, but is slightly larger after inclusion of the BSSE correction. The geometry was not optimized for the large basis calculation but was taken from a combination of the small basis set results and the results for  $\text{Cr}(\text{CO})_6$ . However, a full optimization of the geometry would probably only lead to a small correction to the total binding energy. For example, in  $\text{Cr}(\text{CO})_6$  a Cr–C bond distance which is inaccurate by  $0.03\ a_0$  gives a total energy which is 0.5 kcal/mol higher than the minimum energy, and a C–O bond distance which is in error by  $0.03\ a_0$  gives a total energy which is less than 2 kcal/mol higher. Based on this, we expect that a full optimization of the  $\text{Cr}(\text{CO})_5$  structure would yield less than 2 kcal/mol additional binding energy. We note that there is no direct experimental determination of the total binding energy of  $\text{Cr}(\text{CO})_5$ .

### 3.3.3 The first CO bond dissociation energy of $\text{Cr}(\text{CO})_6$

The results for the first CO bond dissociation energy are given in Table 8. There are two recent experimental determinations, both of which agree on the value of 37 kcal/mol at 298 K [49, 50]. We have corrected these to a  $D_e$  value at 0 K by using harmonic vibrational frequencies computed at the SCF level of theory in the small basis for  $\text{Cr}(\text{CO})_6$  and  $\text{Cr}(\text{CO})_5$  and a standard correction [51] for translational and rotational degrees of freedom ( $\frac{7}{2}RT$  for equation (1)). Although the SCF method does not describe the structure and force constants of these molecules particularly well, the

vibrational correction based on these frequencies is remarkably good. For example, for equation (2) the total correction due to zero-point and vibrational-excitation is 19.7 kcal/mol computed using the experimental frequencies for  $\text{Cr}(\text{CO})_6$  [28, 52] and CO [53], and 18.8 kcal/mol when computed using the SCF frequencies. This agreement is fortuitous, because there is a cancellation of errors between the  $\text{Cr}(\text{CO})_6$  and isolated CO calculations, and between the zero-point and vibrational-excitation corrections. The Cr-C stretch frequencies are too low at the SCF level, leading to increased vibrational-excitation at 298 K (0.5 kcal too high), whereas the C-O stretches are too high (in  $\text{Cr}(\text{CO})_6$ ), leading to a zero-point correction for equation (2) which is 1.4 kcal/mol too small, giving a net error of only 0.9 kcal/mol. The combined error of around 2 kcal/mol is still remarkably small, however, and since we may expect similar results for  $\text{Cr}(\text{CO})_5$ , the correction for equation (1) of 1.6 kcal/mol should be reliable.

For the first bond dissociation energy, the results in the small basis set are already in good agreement with experiment. The CCSD(T) value is almost 8 kcal/mol larger than MCPF, and interestingly the CCSD value is superior to the MCPF value. We recall from § 3.1 that the CCSD method also gave Cr-C bond distances and force constants which were superior to the MCPF values. Thus it seems that the CCSD method, which is not as good as MCPF for isolated CO or the total binding energies of  $\text{Cr}(\text{CO})_6$  and  $\text{Cr}(\text{CO})_5$ , describes the Cr-CO interaction more accurately in these systems, and also yields a more balanced description of  $\text{Cr}(\text{CO})_6$  and  $\text{Cr}(\text{CO})_5$ . This is similar to results found for NiCO and  $\text{Ni}(\text{CO})_2$  previously [9].

After correcting for superposition error (using the indirect method — see § 3.3.1) the CCSD(T) method yields a very good value for the first bond dissociation energy. In the large basis the MCPF approach yields about a 1 kcal/mol increase in the first bond dissociation energy (after correction for BSSE). There are several sources of uncertainty in the first bond dissociation energy. The  $\text{Cr}(\text{CO})_5$  structure was not fully optimized in either basis set, which may reduce the first bond dissociation energy by 1-2 kcal/mol (by increasing the total binding energy of  $\text{Cr}(\text{CO})_5$  — see § 3.3.2). The BSSE correction is somewhat uncertain, as discussed earlier, and the true computed binding energy may be smaller, as indicated by the figures in brackets in Table 8. However, the BSSE correction is relatively small in the large basis, and the MCPF approach yields a very similar first bond dissociation energy in both basis sets, so that this error is probably fairly small. We note that test calculations indicate that differential  $3s3p$  correlation effects between  $\text{Cr}(\text{CO})_6$  and  $\text{Cr}(\text{CO})_5$  are less than 1 kcal/mol. Overall, these uncertainties are small, and an estimated value of

around 38 kcal/mol for the first bond dissociation energy for the CCSD(T) method in the large basis set is not unreasonable and is in very good agreement with the experimental value.

## 4 Conclusions

The geometric structures and energetics of  $\text{Cr}(\text{CO})_6$  and  $\text{Cr}(\text{CO})_5$  were determined at the MCPF, CCSD and CCSD(T) levels of theory. For  $\text{Cr}(\text{CO})_6$ , the structure and force constants for the totally symmetric representation are in good agreement with experimental data once basis set limitations are taken into account. After accounting for  $3s3p$  correlation, a small relativistic effect, and basis set superposition error, the total binding energy of  $\text{Cr}(\text{CO})_6$  is estimated to be around 140 kcal/mol in our largest basis set at the CCSD(T) level of theory, or about 86% of the experimental value. The remaining discrepancy between the experimental and theoretical total binding energy of  $\text{Cr}(\text{CO})_6$  is probably due to limitations in the one-particle basis, rather than limitations in the correlation treatment, and an additional  $d$  function and an  $f$  function on each C and O are needed to obtain quantitative results. This is underscored by the fact that even using a very large primitive set (1042 primitive functions contracted to 300 basis functions), the superposition error for the total binding energy of  $\text{Cr}(\text{CO})_6$  is 22 kcal/mol at the MCPF level of treatment. In contrast, the first bond dissociation energy of  $\text{Cr}(\text{CO})_6$  is very well described at the CCSD(T) level of theory, due to a cancellation of basis set incompleteness errors for  $\text{Cr}(\text{CO})_6$  and  $\text{Cr}(\text{CO})_5$ , and our best estimated value of 38 kcal/mol is within the experimental error bars.

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Table 1: Optimized bond lengths for  $\text{Cr}(\text{CO})_6$ , valence only ( $a_0$ )

	$r(\text{Cr-C})$	$r(\text{C-O})$
Small basis		
SCF	3.775	2.142
MCPF	3.692	2.215
CCSD	3.684	2.207
CCSD(T)	3.664	2.227
Large basis		
MCPF	3.666	2.165
Expt <sup>a</sup>	3.616	2.154

<sup>a</sup> Bond distances are from Jost *et al.* [40]. See also Rees and Mitschler [41].

Table 2: Force constants for  $\text{Cr}(\text{CO})_6$ , valence only ( $\text{aJ}/\text{\AA}^2$ )<sup>a</sup>

	$F_{11}$	$F_{22}$	$F_{12}$
Small basis			
MCPF	15.18	2.06	0.31
CCSD	15.70	2.21	0.31
CCSD(T)	14.44	2.24	0.27
Large basis			
MCPF	18.75	2.32	0.23
Expt <sup>b</sup>	18.11	2.44	0.38
Expt Error	$\pm 0.16$	$\pm 0.02$	$\pm 0.13$

<sup>a</sup> In the notation of Jones *et al.* [28].  $F_{11}$  is for the totally symmetric C–O stretch,  $F_{22}$  is for the totally symmetric Cr–C stretch and  $F_{12}$  is the coupling term.

<sup>b</sup> Jones *et al.* [28].

Table 3: Cr(CO)<sub>5</sub> bond distances and angles, valence only (a<sub>0</sub> and degrees)

	$r(\text{Cr-C})_{ax}$	$r(\text{C-O})_{ax}$	$r(\text{Cr-C})_{eq}$	$r(\text{C-O})_{eq}$	$\angle \text{C}_{ax}\text{CrC}_{eq}$	$\angle \text{CrC}_{eq}\text{O}_{eq}$
<sup>1</sup> A <sub>1</sub> C <sub>4v</sub>						
SCF	3.734	2.144	3.772	2.146	92.5	179.4
MCPF	3.624	2.215 <sup>a</sup>	3.708	2.215 <sup>a</sup>	92.5 <sup>a</sup>	179.4 <sup>a</sup>
CCSD	3.567	2.220 <sup>a</sup>	3.670 <sup>a</sup>	2.220 <sup>a</sup>	92.5 <sup>a</sup>	179.4 <sup>a</sup>
CCSD(T)	3.554	2.220 <sup>a</sup>	3.670 <sup>a</sup>	2.220 <sup>a</sup>	92.5 <sup>a</sup>	179.4 <sup>a</sup>
<sup>3</sup> A <sub>2</sub> ' D <sub>3h</sub>						
SCF	3.737	2.153	3.927	2.135		

<sup>a</sup> Not optimized (see text)

Table 4: Basis set superposition errors for various  $\text{Cr}(\text{CO})_6$  fragments (kcal/mol)

	SCF	MCPF
(1) Small basis, valence only		
Cr + $(\text{CO})_6$ (ghost)	0.6	3.1
$(\text{CO})_6$ + Cr (ghost)	8.6	24.5
Sum	9.2	27.6
(2) Large basis, valence only		
Cr + $(\text{CO})_6$ (ghost)	0.6	2.5
$(\text{CO})_6$ + Cr (ghost)	4.7	12.9
Sum	5.3	15.4
(3) Large 3s3p basis, valence only		
Cr + $(\text{CO})_6$ (ghost)	0.0	0.8
$(\text{CO})_6$ + Cr (ghost)	8.0	21.1
Sum	8.0	21.9
(4) Large 3s3p basis, 3s3p + valence		
Cr + $(\text{CO})_6$ (ghost)	0.0	1.5
$(\text{CO})_6$ + Cr (ghost)	8.0	21.1
Sum	8.0	22.6

Table 5: Basis set superposition errors for various  $\text{Cr}(\text{CO})_5$  fragments, valence only (kcal/mol)

	SCF	MCPF
(1) Small basis		
Cr + $(\text{CO})_5$ (ghost)	0.5	2.8
$(\text{CO})_5$ + Cr (ghost)	7.1	19.2
Sum	7.6	22.0
(2) Small basis		
$\text{Cr}(\text{CO})_5$ + CO (ghost)	1.8	4.4
CO + $\text{Cr}(\text{CO})_5$ (ghost)	2.8	6.0
Sum	4.6	10.4
(3) Large basis		
Cr + $(\text{CO})_5$ (ghost)	0.5	2.3
$(\text{CO})_5$ + Cr (ghost)	4.1	10.8
Sum	4.6	13.1

Table 6: Total CO binding energies for  $\text{Cr}(\text{CO})_6$  (kcal/mol)

	BE	BE/ $N_{\text{CO}}$	BE-BSSE	(BE-BSSE)/ $N_{\text{CO}}$
Small basis, valence only				
MCPF	109.5	18.3	81.9	13.6
CCSD	103.3	17.2	75.7	12.6
CCSD(T)	139.4	23.2	111.8	18.6
Large basis, valence only				
MCPF	100.0	16.7	84.6	14.1
CCSD <sup>a</sup>	95.7	16.0	80.4	13.4
CCSD(T) <sup>a</sup>	136.4	22.7	121.0	20.2
Large 3s3p basis, valence only <sup>b</sup>				
MCPF	112.5	18.8	90.7	15.1
Large 3s3p basis, 3s3p + valence <sup>b</sup>				
MCPF	117.1	19.5	94.5	15.8
Expt	162 <sup>c</sup>	27	162	27

<sup>a</sup> Geometry not optimized (see text).  $r(\text{Cr-C})=3.638 a_0$ ,  $r(\text{C-O})=2.177 a_0$

<sup>b</sup> At the large basis MCPF geometry

<sup>c</sup> The experimental binding energy corresponding to  $D_0^{298}$  is 153 kcal/mol, from Pittam *et al.* [54]. The value given here corresponds to  $D_e$ , derived using the data summarized by Pilcher *et al.* [52]

Table 7: Total CO binding energies for Cr(CO)<sub>5</sub>, valence only (kcal/mol)

	BE	BE/N <sub>CO</sub>	BE-BSSE	(BE-BSSE)/N <sub>CO</sub>
Small basis				
MCPF	74.8	15.0	52.8	10.6
CCSD	65.1	13.0	43.1	8.6
CCSD(T)	96.7	19.3	74.7	15.0
Large basis <sup>a</sup>				
MCPF	67.8	13.6	54.7	10.9

<sup>a</sup> Geometry not optimized (see text).  $r(\text{Cr-C})_{ax}=3.600 \text{ a}_0$ ,  $r(\text{Cr-C})_{eq}=3.680 \text{ a}_0$ , and  $r(\text{C-O})_{ax}=r(\text{C-O})_{eq}=2.165 \text{ a}_0$

Table 8: First CO binding energy of  $\text{Cr}(\text{CO})_6$ , valence only (kcal/mol)

$\text{Cr}(\text{CO})_6 \rightarrow \text{Cr}(\text{CO})_5 + \text{CO}$		
	$\Delta E$	$\Delta E\text{-BSSE}^{\text{a}(\text{b})}$
Small basis		
MCPF	34.8	29.1 (24.3)
CCSD	38.8	32.6 (27.8)
CCSD(T)	42.7	37.1 (32.3)
Large basis		
MCPF	32.3	30.0
Experimental data		
$D_0^{298}$	37	37
$D_e$	38.6 <sup>c</sup>	38.6
Expt Error	$\pm 5^{\text{d}}, \pm 2^{\text{e}}$	$\pm 5, \pm 2$

<sup>a</sup> Corrected using the indirectly computed BSSE values (see text)

<sup>b</sup> Corrected using the directly computed BSSE values (see text)

<sup>c</sup> Correction of 1.6 kcal/mol based on theoretical results (see text)

<sup>d</sup> Bernstein *et al.* [49].

<sup>e</sup> Lewis *et al.* [50].

## Appendix

For reference purposes, in Table 9 we give the total energies necessary for the superposition error calculations. In Table 10 we give the total energies for various  $\text{Cr}(\text{CO})_6$  calculations, including the exact geometries used. The number of configurations in the wavefunction is also given. The total energies of the isolated CO molecules were given previously [39]. Finally, in Table 11 we give the exponents and contraction coefficients for the large  $3s3p$  chromium atom basis.

Table 9: Total energies for BSSE calculations (a.u.)

	SCF	MCPF
(1) Small basis, valence only <sup>a</sup>		
Cr + (CO) <sub>6</sub> (ghost)	-1043.30325162	-1043.36680779
Cr	-1043.30227534	-1043.36188023
(CO) <sub>6</sub> + Cr (ghost)	-676.09997013	-677.52038240
(CO) <sub>6</sub>	-676.08622041	-677.48125821
(2) Large basis, valence only <sup>b</sup>		
Cr + (CO) <sub>6</sub> (ghost)	-1043.30325705	-1043.39812877
Cr	-1043.30227534	-1043.39413050
(CO) <sub>6</sub> + Cr (ghost)	-676.58083795	-678.61170166
(CO) <sub>6</sub>	-676.57336447	-678.59116206
(3) Large 3s3p basis, valence only <sup>c</sup>		
Cr + (CO) <sub>6</sub> (ghost)	-1043.35596972	-1043.45792578
Cr	-1043.35594229	-1043.45664455
(CO) <sub>6</sub> + Cr (ghost)	-676.59006301	-678.62268211
(CO) <sub>6</sub>	-676.57728805	-678.58910199
(4) Large 3s3p basis, 3s3p + valence <sup>c</sup>		
Cr + (CO) <sub>6</sub> (ghost)	-1043.35596972	-1043.79914043
Cr	-1043.35594229	-1043.79671781
(CO) <sub>6</sub> + Cr (ghost)	-676.59006301	-678.62268211
(CO) <sub>6</sub>	-676.57728805	-678.58910199

<sup>a</sup>  $r(\text{Cr-C})=3.684$  a.u.,  $r(\text{C-O})=2.207$  a.u.

<sup>b</sup>  $r(\text{Cr-C})=3.696$  a.u.,  $r(\text{C-O})=2.180$  a.u.

<sup>c</sup>  $r(\text{Cr-C})=3.666679456$  a.u.,  $r(\text{C-O})=2.164607427$  a.u.

Table 10: Total energies and number of configurations for  $\text{Cr}(\text{CO})_6$  (a.u.)

	$r(\text{Cr-C})$	$r(\text{C-O})$	E	#config
Small basis, valence only				
SCF	3.675000000	2.215000000	-1719.38028800	-
MCPF	3.700000000	2.215000000	-1721.08354571	1550884
CCSD	3.675000000	2.200000000	-1721.06032683	1550884
CCSD(T)	3.675000000	2.230000000	-1721.19228447	-
Large basis, valence only				
SCF	3.638099092	2.177373367	-1719.85243699	-
MCPF	3.650000000	2.160000000	-1722.21948766	3229861
CCSD	3.638099092	2.177373367	-1722.18375812	3229861
CCSD(T)	3.638099092	2.177373367	-1722.33885385	-
Large 3s3p basis, valence only				
SCF	3.666679456	2.164607427	-1719.92269380	-
MCPF	3.666679456	2.164607427	-1722.30216532	4223071
Large 3s3p basis, 3s3p + valence				
SCF	3.666679456	2.164607427	-1719.92269380	-
MCPF	3.666679456	2.164607427	-1722.64951637	5321953

Table 11: Large 3s3p basis exponents and contraction coefficients

Exponents	Contraction coefficients								
	s functions								
3638305.	0.000009	-0.000003	0.000001	0.0	0.0	0.0	0.0	0.0	0.0
544822.5	0.000068	-0.000020	0.000007	0.0	0.0	0.0	0.0	0.0	0.0
123986.8	0.000359	-0.000108	0.000039	0.0	0.0	0.0	0.0	0.0	0.0
35117.88	0.001512	-0.000454	0.000166	0.0	0.0	0.0	0.0	0.0	0.0
11456.10	0.005476	-0.001651	0.000602	0.0	0.0	0.0	0.0	0.0	0.0
4135.206	0.017557	-0.005342	0.001954	0.0	0.0	0.0	0.0	0.0	0.0
1612.295	0.050084	-0.015606	0.005716	0.0	0.0	0.0	0.0	0.0	0.0
668.0686	0.124182	-0.040792	0.015060	0.0	0.0	0.0	0.0	0.0	0.0
290.5773	0.250869	-0.092401	0.034485	0.0	0.0	0.0	0.0	0.0	0.0
131.3286	0.359000	-0.167315	0.064515	0.0	0.0	0.0	0.0	0.0	0.0
60.78704	0.275336	-0.187672	0.075767	0.0	0.0	0.0	0.0	0.0	0.0
27.44308	0.065683	0.045233	-0.018997	0.0	0.0	0.0	0.0	0.0	0.0
13.08202	-0.001163	0.510933	-0.293025	0.0	0.0	0.0	0.0	0.0	0.0
6.244786	0.001961	0.506228	-0.455426	0.0	0.0	0.0	0.0	0.0	0.0
2.753437	0.000000	0.000000	0.000000	1.0	0.0	0.0	0.0	0.0	0.0
1.298441	0.000000	0.000000	0.000000	0.0	1.0	0.0	0.0	0.0	0.0
0.572030	0.000000	0.000000	0.000000	0.0	0.0	1.0	0.0	0.0	0.0
0.125502	0.000000	0.000000	0.000000	0.0	0.0	0.0	1.0	0.0	0.0
0.062470	0.000000	0.000000	0.000000	0.0	0.0	0.0	0.0	1.0	0.0
0.028354	0.000000	0.000000	0.000000	0.0	0.0	0.0	0.0	0.0	1.0

Table 11: cont. Large 3s3p basis exponents and contraction coefficients

Exponents		Contraction coefficients						
		<i>p</i> functions						
6399.333	0.000181	-0.000064	0.000000	0.0	0.0	0.0	0.0	0.0
1515.982	0.001587	-0.000562	0.000000	0.0	0.0	0.0	0.0	0.0
491.9534	0.008813	-0.003146	0.000000	0.0	0.0	0.0	0.0	0.0
187.3677	0.036027	-0.013003	0.000000	0.0	0.0	0.0	0.0	0.0
78.82903	0.111802	-0.041650	0.000000	0.0	0.0	0.0	0.0	0.0
35.40597	0.251912	-0.097437	0.000000	0.0	0.0	0.0	0.0	0.0
16.51195	0.380832	-0.157341	0.000000	0.0	0.0	0.0	0.0	0.0
7.895010	0.310519	-0.115133	0.000000	0.0	0.0	0.0	0.0	0.0
3.713305	0.000000	0.000000	1.000000	0.0	0.0	0.0	0.0	0.0
1.724220	0.000000	0.000000	0.000000	1.0	0.0	0.0	0.0	0.0
0.772673	0.000000	0.000000	0.000000	0.0	1.0	0.0	0.0	0.0
0.319507	0.000000	0.000000	0.000000	0.0	0.0	1.0	0.0	0.0
0.127803	0.000000	0.000000	0.000000	0.0	0.0	0.0	1.0	0.0
0.051121	0.000000	0.000000	0.000000	0.0	0.0	0.0	0.0	1.0
		<i>d</i> functions						
177.0182	0.000907	0.000000	0.000000	0.0	0.0	0.0		
52.85958	0.007660	0.000000	0.000000	0.0	0.0	0.0		
20.09064	0.034236	0.000000	0.000000	0.0	0.0	0.0		
8.416376	0.104090	0.000000	0.000000	0.0	0.0	0.0		
3.759310	0.223015	0.000000	0.000000	0.0	0.0	0.0		
1.706759	0.000000	1.000000	0.000000	0.0	0.0	0.0		
0.762211	0.000000	0.000000	1.000000	0.0	0.0	0.0		
0.327886	0.000000	0.000000	0.000000	1.0	0.0	0.0		
0.129421	0.000000	0.000000	0.000000	0.0	1.0	0.0		
0.045794	0.000000	0.000000	0.000000	0.0	0.0	1.0		
		<i>f</i> functions						
2.7313203	0.486200	1.085700	-2.379100					
2.0000000	-0.024700	-0.472000	2.079900					
0.9795143	0.471700	0.175500	0.661700					
0.4194397	0.294700	-0.865300	-0.832900					